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A laboratory study on the effect of sulfuric acid on charge transfer during ice-graupel collision

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Abstract : Charge transfer experiments were carried out inside a walk-in cold room to investigate the sign and magnitude of charge that is transferred to the graupel (soft-hail) during collision between ice crystal and graupel. Different concentrations (0%, 25%, and 50%) of aqueous solution of sulfuric acid were used to produce cloud during the experiments. A cloud of supercooled droplets is formed inside the cloud chamber by heating the aqueous solution of sulfuric acid, and the ice crystal formation in the cloud is initiated by momentarily introducing a metal rod dipped in liquid nitrogen into the cloud. It is observed that the magnitude of charge transfer increases with concentration of sulfuric acid in the aqueous solution. If the aqueous solution contains 25% and 50% of sulfuric acid by weight, a coat of dark film is seen on the crystal surface. Due to this film, the crystals boundaries are no longer sharp and well defined like that observed in the crystals produced in pure water cloud. It is suggested that during collision between ice crystal and graupel, this film could be transferred to the graupel resulting in higher values of charge transfer.

Keywords : Thunderstorm electrification, sulfuric acid, graupel, charge transfer.

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1. Introduction

Acid deposition and acid rain from atmosphere present a serious environmental problem. Acid precipitation is a mixture of strong acid like sulfuric acid, nitric acid and hydrochloric acid. pH value has been found to be around 2.8 in acid rain events and near Smoking Hills, Canada, a low value of 1.8 has been reported [1]. Pollutants which could be gases or particles are moved by the air currents, they can undergo complex chemical and physical transformations, forming products that return to the Earth's surface as wet or dry deposition. Sulfur dioxide can be converted into sulfuric acid in the atmosphere and this acid may be incorporated into precipitation and brought down to the Earth's surface as acid rain [2]. Sulfur dioxide is converted into sulfate aerosols when emitted into the air. Sulfate aerosols are an important source of nuclei around which cloud droplets can condense. Studies have shown that the pollutants can greatly influence the cloud microphysics. The evaporation rate of liquid or solid can be retarded by the formation of a foreign layer on the surface. Chemical materials can affect the growth of ice crystals by changing the evaporation rate [3–5] or by altering the structure of ice crystals [6–8]. Trace chemicals can deposit on the ice surface and can be incorporated into growing ice particles with high concentrations. A detailed microphysical understanding of crystal formation in polluted clouds is needed. Also the participation of these crystals in collision with graupel is important to describe the charging mechanisms in polluted cloud.

It is widely accepted that the development of electric field in the thunderstorm is associated with a non-inductive charging process involving rebound collisions between soft-hail (graupel) and ice crystal [9–16]. The results of the experiments indicate that if the supercooled water droplets and ice crystals co-exist in the cloud, large amounts of charges are separated during collision. The sign and magnitude of charge transfer resulting from rebounding collisions between ice-ice/soft-hail (graupel) depends on temperature, liquid water content, ice crystal

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size, rime accretion rate (RAR), impact velocity, surface properties of ice, and chemical impurities of the cloud water [9,17–20].

Experimental results on charge transfer for chemically polluted clouds are found in literature, but results are not sufficient to explain the charging mechanism and some of them are conflicting. Jayaratne [20] reported that ice crystals interacting with a simulated graupel pellet charge the graupel negatively when the cloud droplets contained traces of sodium chloride. He also found that if ammonium salt is present in the droplet then graupel is charged positively.

Takahashi [21] also conducted charge transfer experiments with aqueous solution of sodium chloride (NaCl) and ammonium sulfate ($(NH_4)_2SO_4$). At temperature –20°C when there is no ice crystal in the chamber, the target was only slightly electrified. It charged negatively for sodium chloride solution and positively for ammonium sulfate solution. But in presence of ice crystals and at same temperature, the target was strongly electrified negatively irrespective of the solution used.

The sign and magnitude of charge transfer during the collisions depend on the surface property of the ice and soft hail [11,13–15,22,23]. A liquid like layer is present over the surface of ice crystal due to surface melting [14]. During the collisions, this liquid-like layer is exchanged between the two colliding bodies resulting in a redistribution of the dissociated ions and leading to a transfer of charge after the collision. However, surface melting is generally observed near the melting point. In laboratory experiments, charge is found to be transferred during the collisions even at –38°C [13]. But at very low temperatures (–38°C), the surface melted liquid-like layer is not supposed to exist. Sommer and Levin [24] reported that the thickness of the liquid-like layer decreases with temperature, from 32 nm at –1°C to 1 nm at –38.5°C, and the charge transfer could depend on the thickness of the liquid-like layer on the ice crystal surface. They also observed that there is practically no charging at temperatures below –38°C [24]. If the ice crystals are formed from sulfuric acid/water mixture, dark fuzzy spots are found on the surface of ice crystals and this could be film of acid on the surface [25].

Keith and Saunders [13] discussed a new mechanism of charge transfer related to the dislocation over the crystal surface. The dislocation density on the ice and the charges associated with them have been found experimentally [26,27]. Dislocation density on the ice crystal is a function of growth rate, which in turn, is a function of the cloud temperature and liquid water content. The maximum growth rate of crystal occurs at a temperature of –12°C [13]; therefore, the dislocation production rate at this temperature may also be maximum.

Due to the random impact and rapid freezing of supercooled water droplets during riming, various defects could be formed over the surface. As the process of riming continues, the surface structure of ice will tend to deviate from its perfect crystalline structure. Datta *et al* [28] suggested a new concept of quasi-solid layer (QSL) for this type of structure over the surface of the ice crystals. This QSL is responsible for charge transfer during the collisions between ice crystal and graupel. The magnitude of the charge transfer depends on the contact area and depth of the quasi-solid layer (QSL).

2. Experimental methodology

Experiments were conducted in the glass chamber which is kept in a walk-in cold room which can reach a lowest temperature of –30°C and has been described earlier [29]. Figure 1 shows the detailed view of experimental arrangement inside the cold room. A solution of sulfuric acid and water in definite proportion (25% and 50% sulfuric acid by weight in water) is heated at a controlled rate to produce vapor. This vapor is then introduced into the spherical glass chamber, and when a steady state temperature is reached, the cloud is seeded with a rod dipped in liquid nitrogen. This causes adiabatic cooling in the region surrounding the rod. The ice crystal formation is initiated by homogeneous nucleation followed by other ice multiplication processes.

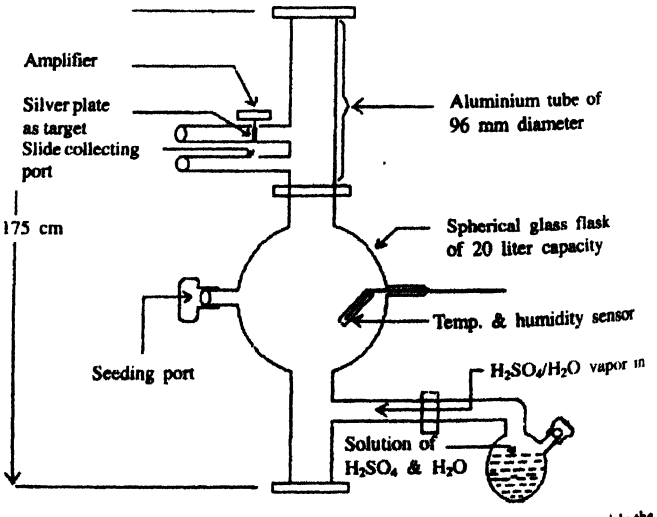

Figure 1. Schematic representation of experimental arrangement inside the cold room for charge transfer experiment in sulfuric acid cloud.

There are two extended tubes to the side of the upper limb of experimental chamber (top one is made of aluminum and the lower one is made of glass) with the separation of 10 cm. The diameter (inner) of both the tubes is 2.7 cm. A silver target of 18 mm × 4 mm is kept on the top aluminum tube and is directly connected to the input of charge amplifier. The silver target is chemically cleaned to prevent oxide formation. The lower extended tube (glass tube) is used for collecting crystals on the formvar coated microscope slide and is of the same size as that of silver target. Both tubes are connected to a suction pump through a glass valve.

Before starting the charge transfer experiment, suction pump is used to suck the mixed phase (ice crystals and droplets) cloud through the side extended tube to make rime (soft-hail/graupel) on the silver target. Ice crystals in the cloud are allowed to grow to a reasonably large size and at the same time, the number of ice crystals also becomes few. The cloud of supercooled drops and ice crystals is then drawn through the tubes with a constant speed of 2.9 ms^{-1}. Inside the upper tube, the ice crystals collide with rimed target and rebound from the target. During the collision, ice crystals transfer charges to the rimed target. A charge amplifier connected to the silver target measures the charges and has a calibration factor of 1 mV for a charge transfer of 10 fC (10^{-15} C). The output after further amplification is recorded on a computer using a 12 bit A/D card. Figure 2 shows a typical record of the obtained signal.

Microscope slide coated with a solution of chloroform and formvar is kept vertically inside the lower tube to collect the ice crystals on it for analysis of size and shape. During experiments, the precipitation falling down are collected in a small beaker kept at the bottom of the chamber. pH value of this solution is measured by pH meter. It is found that pH value for clouds which were formed from aqueous solution containing 25% sulfuric acid is 2.8 (± 0.1) and that for 50% sulfuric acid is 1.95 (± 0.1).

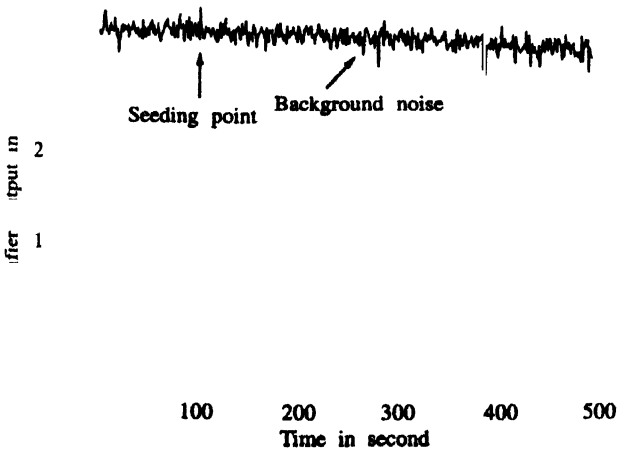

Figure 2. Shows the output of charge amplifier recorded on the computer. The cloud temperature was –11.2°C. This charge transfer signal has been recorded when 28 ice crystalls of 80 μm, collide and rebound from the target.

3. Results

Charge transfer values have also been obtained when the cloud is formed from pure water only. This will serve as a reference against which we will compare the results of the charge transfer experiments done with sulfuric acid/water mixture. Figure 3 shows the charge transfer values against ice crystal size when the cloud was formed by heating pure water. It is seen that the charge transfer values increase with increasing size of ice crystals.

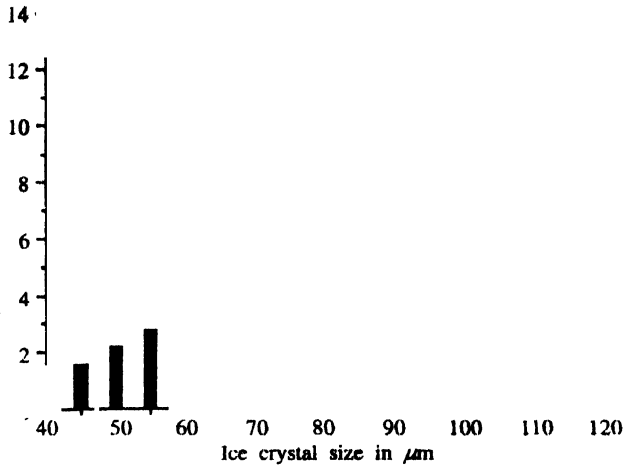

Figure 3. Shows charge transfer values as a function of ice crystal size for pure water cloud.

Figure 4 shows the charge transfer values against ice crystal size when the cloud was formed by heating aqueous solution containing 25% of sulfuric acid. It is seen that the charge transfer values for ice crystal sizes till 100 μm, are about the same as those seen in Figure 3 for the case of pure water. For crystal sizes larger than 100 μm, the charge transfer values for cloud formed from 25% sulfuric acid is more. For crystal sizes of about 115 μm, the increase in charge transfer is about 7 fc.

Figure 5 shows the charge transfer values against ice crystal size when the cloud was formed by heating aqueous solution containing 50% of sulfuric acid. Here, it is seen that for all size bins of ice crystals, the charge transfer value is more than the pure water case. For crystal sizes of about 155 μm, the increase in charge transfer is about 10 fc.

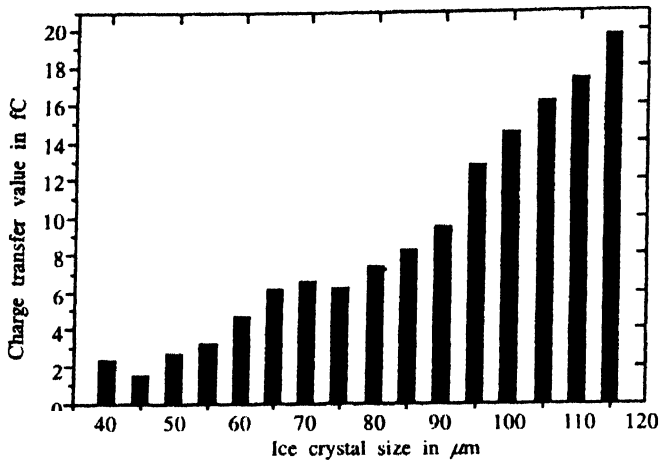

Figure 4. Charge transfer values as function of ice crystal size. The cloud was made by heating aqueous solution containing 25% of sulfuric acid (by weight).

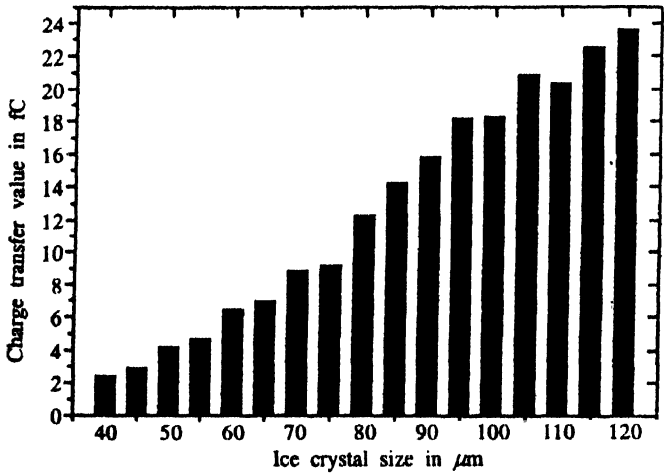

Figure 5. Charge transfer values as a function of ice crystal size. The cloud was made by heating aqueous solution containing 50% of sulfuric acid (by weight).

As reported earlier [25], fuzzy dark spots have been found on the surface of ice crystal and which is believed to be acid film. The thickness of this acid film over the surface of ice crystal also increases with the increasing concentration of sulfuric acid in the aqueous solution. Ice crystals from 50% H_2SO_4 cloud are darker as compared to the crystals from 25% acid clouds. Figure 6 shows (a) ice crystals collected from pure water cloud, (b) ice crystals collected from cloud which has been formed by heating aqueous solution containing 25% sulfuric acid and (c) from 50% sulfuric acid.

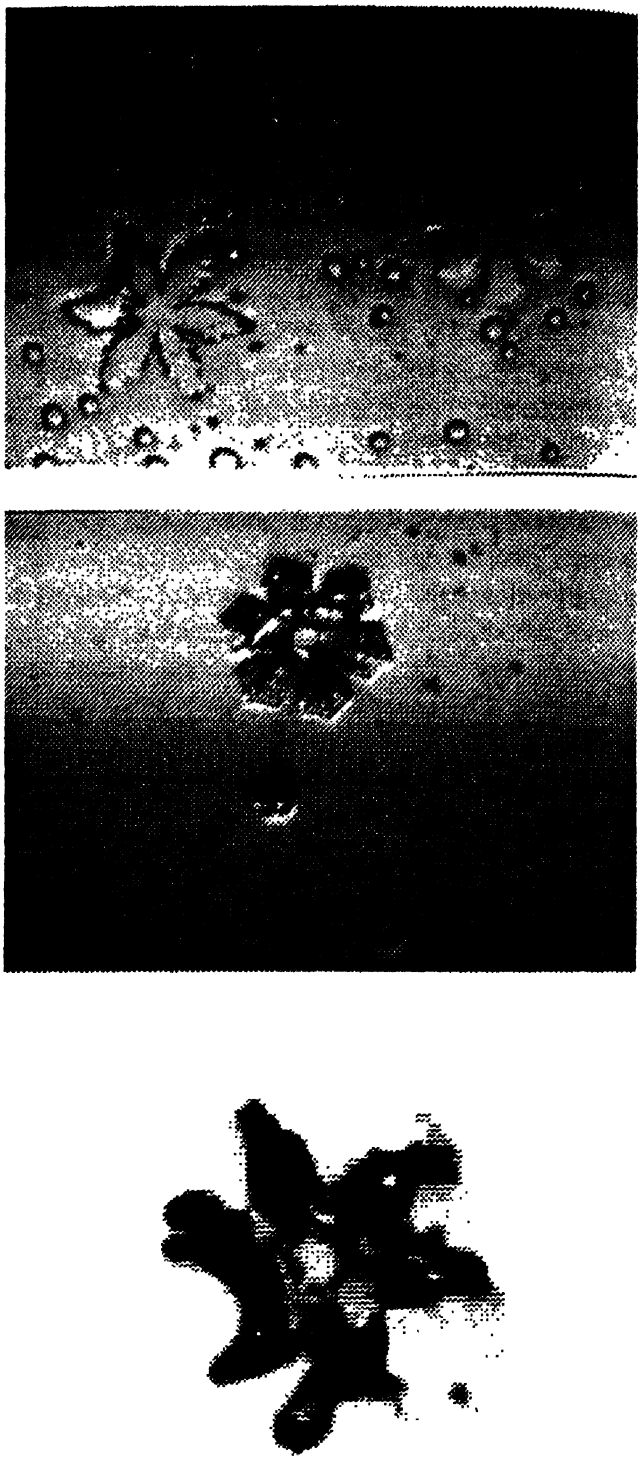

Figure 6. Shows (a) ice crystals collected from pure water cloud, (b) ice crystals collected from cloud which was formed by heating aqueous solution containing 25% sulfuric acid and (c) from 50% sulfuric acid.

4. Discussion

In the present experiments, we have observed the charge transfer values during ice crystal and hail (graupel) collision increases with the concentration of sulfuric acid in the cloud. The sign of charge that is transferred to the graupel in the temperature range −9 to −14°C, is always positive for both pure water cloud and also for that

containing sulfuric acid. It has also been found that there is a film of acid on the surface of ice crystals formed in acid clouds. The thickness of this film increases with acid concentration. It is proposed that this film of acid could be quasi liquid-like and during the collisions between ice and graupel, this quasi liquid-like layer is being transferred to the graupel resulting in higher charge transfer.

Research carried out mostly in the arctic, shows that sulfuric acid dominates 60% of the total sulfate mass in the aerosol particles [30]. Thin film of sulfuric acid has been found to envelope more than 50% of insoluble particles in that region [31,32]. Laboratory experiments show that the presence of sulfuric acid can reduce the homogenous freezing temperatures of such droplets [33]. As various ice multiplication mechanisms are operating inside the cloud, if such a droplet containing sulfuric acid freezes, it is possible that the sulfuric acid will be ejected to the surface to form a film [5,25].

The possible influence of trace chemicals, in particular sulfate and nitrate, on growth and lifetime of ice crystals has been studied theoretically by Chen and Crutzen [5]. The study shows that the solute accumulated on the surface of ice particles during evaporation, tends to form a layer of concentrated solution, which alters the equilibrium vapour pressure and thus affects the evaporation of ice particles. Hallett [34] suggested that the surface of the ice particle is probably important in chemical reactions and charge separation processes.

Baker and Dash [14] suggested that the charge transfer during the collisions is associated with mass transfer between ice particles. They mentioned that there is a flow of surface material from warm to cold, from regions of high surface curvature to those of smaller curvature, and from regions of high vapour growth to regions of lower growth or evaporation. The particle with thicker layer on the surface will loose mass and the other with thinner layer, will gain mass. The former particle will thereby acquire a negative charge and latter particle, a positive charge. The sign of the charge transfer will then be a function of relative growth rate. The magnitude of charge transfer is dependent on the depth of layer on crystal surface. In our experiments, acid film on the surface of crystal could be thicker compared to that on graupel. During collision, it is possible that ice crystal would transfer mass to the graupel resulting in positive charging of target.

Jayaratne [20] performed charge transfer experiments with chemically polluted clouds. He suggested that the impurity ions in the ice target are controlling the direction of charge transfer. During freezing, there is selective incorporation of ions into ice. In case of NaCl, Cl^- ion is more readily accepted by the ice than the Na^+ ion [35]. NaCl provides Na^+ ions close to the surface and cannot be incorporated into the bulk ice, thus resulting in negative charge transfer to the ice target when particles rebound off.

The sulfuric acid concentration used in the present experiments may be too high as compared to the normal acid rain events; it may be applicable only to clouds producing extreme acid rain events. Due to stringent environmental pollution norms, extreme acid rain events may not occur too frequently. However, the results of our experiments can be used to explain the vigorous lightning activity observed in volcanic clouds. From the Pinatubo volcanic eruptions, it is known that the sulfuric acid content in drops is of the same order as in the present laboratory experiments [36]. Measurements of electric fields and charges lowered during lightning discharges from volcanic clouds carried out earlier [37], does show high values of potential gradient at the ground.

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